

THEORETICAL STUDIES OF INTERSTELLAR PROCESSES

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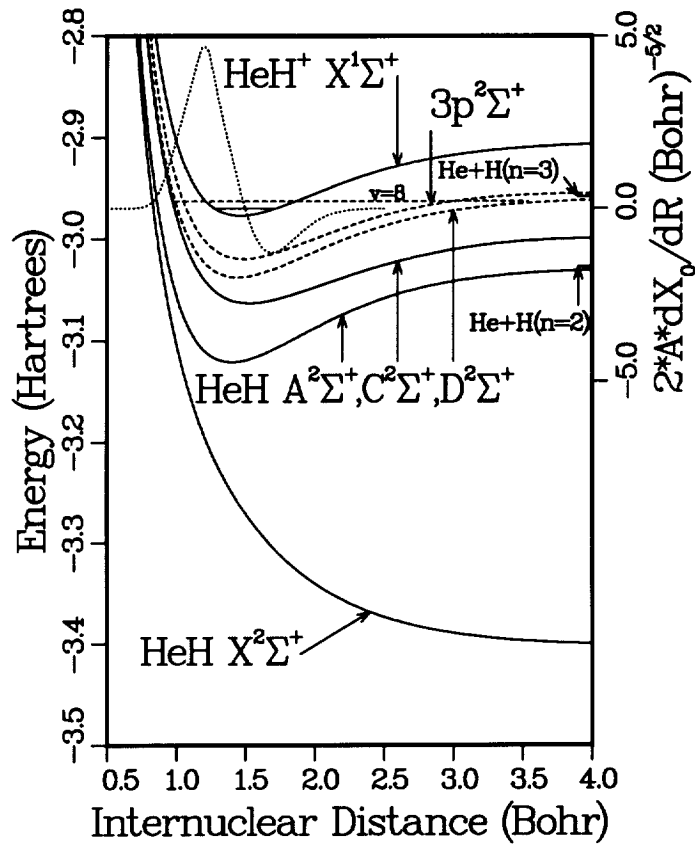
## A. Progress Under NASA Grant NAGW 2832

We have been studying the dissociative recombination (DR) of  $\text{HeH}^+$  with an electron with the goal of calculating accurate cross sections and rate coefficients to allow for the accurate modelling of the abundance of  $\text{HeH}^+$  in planetary nebulae and supernova envelopes. A unique feature of the  $\text{HeH}$  potential curves is that none of the neutral states cross the ion curve. This required a new approach to the calculation of DR cross sections and rate coefficients that had not yet appeared in the literature. Because of the lack of a potential curve crossing, the initial electron capture occurs by Born-Oppenheimer breakdown, i.e. by the interaction of the motion of the incoming electron with the nuclear motion. This same mechanism also drives DR in  $\text{H}_3^+$  and the methods developed and described below for  $\text{HeH}^+$  DR will be used for the future calculation of  $\text{H}_3^+$  DR.

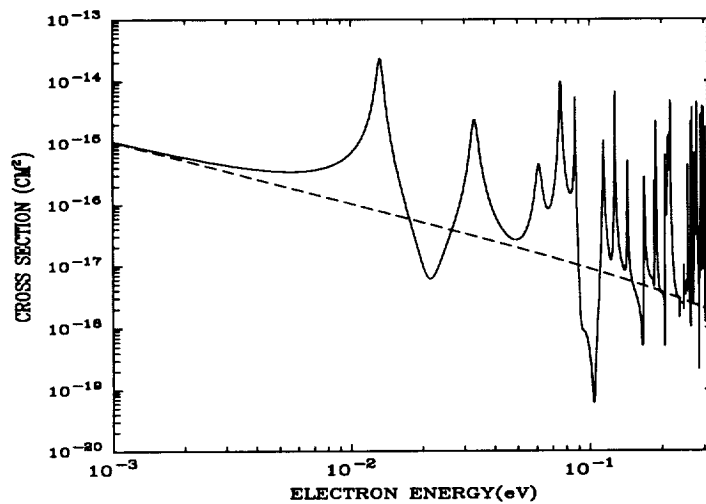
### 1. Potential Energy Curves

Under current NASA support, potential curves for the ground state of  $\text{HeH}^+$  and for the neutral states that are relevant to DR have been calculated using large scale Gaussian basis sets and multireference configuration interaction (CI) wave functions. The wave functions were calculated using atom centered Gaussian basis sets. At both the He and the H, a  $[4s,3p,2d]$  contracted basis set was used supplemented with a single  $4f$  primitive function. On the H, three diffuse  $s$  functions and four diffuse  $p$  functions were added for the description of the Rydberg states. The orbitals were determined in Self Consistent Field (SCF) calculations. A reference set of configurations for a CI wave function was generated by taking all single and double excitations in the space of the lowest energy  $p_x$  and  $p_y$  orbitals and the six lowest energy  $s$  orbitals. The CI was generated by taking all single and double excitations from each member of the reference set. For these small systems it is possible to calculate exceedingly accurate potential curves and the curves reported here are the most accurate  $\text{HeH}$  curves calculated to date. The calculated  $\omega_e$  and  $\omega_e x_e$  values for the ion differ from the experimental values by only  $7\text{cm}^{-1}$ . The  $R_e$  values differ by only  $0.0008a_0$  and the dissociation energies ( $D_e$ ) differ by only  $0.0016\text{eV}$  from experiment. For the A and  $\text{C}^2\Sigma^+$  states of  $\text{HeH}$ , the  $\omega_e$  values differ from the experimental values by less than  $19\text{cm}^{-1}$ . For the A state, the calculated  $R_e$  agrees with the experimental value to 4 decimal places. The calculated  $R_e$  for the C state is  $0.0036a_0$  smaller than the experimental value. The energy differences between the bottom of the calculated ion well and the bottom of the A, C, and D state wells differ from the experimental values by only 198, 86 and  $97\text{cm}^{-1}$  respectively. These highly accurate results are needed to calculate accurate cross sections and rates. The calculated potential curves are shown in Figure 1.

As discussed above, there are no dissociative potential curves that cross the ion. Energetically however, there are three states that can provide routes for DR. These are the ground state and the A and C Rydberg states. The latter two states dissociate to the  $\text{He}+\text{H}(n=2)$  limit which is  $1.55\text{eV}$  below the  $v=0$  level of the ion. An electron can be captured by  $v=0$   $\text{HeH}^+$  directly into the X, A, or C states followed by dissociation along these states. Indirect recombination may also occur in which the electron is captured initially into a vibrationally excited Rydberg state. The



**Figure 1.** The calculated HeH dissociative potential energy curves (solid), the  $n=3$  Rydberg states (dashed) and the  $\text{HeH}^+$  ground state (solid) with the  $v=0$  level are shown.



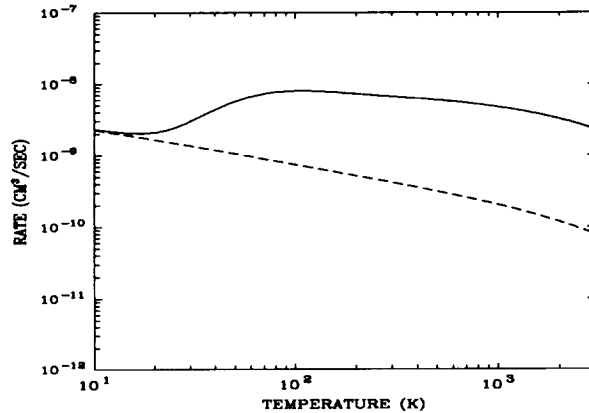
**Figure 2.** The calculated direct (dashed line) and full (solid line) cross sections for  $^4\text{HeH}^+$  DR.

Rydberg state can autoionize or can be predissociated by the X, A, or C states. For the low energy electrons, the D and  $3p^2\Sigma^+$  states (with principal quantum number  $n=3$ ) are the lowest Rydberg states that can be intermediate states in indirect recombination. For the D and  $3p$  states, vibrational levels with  $v=6$  and  $v=4$  respectively lie above the  $v=0$  level of the ion and will be the origin of structure in the DR cross section. For higher  $n$  states, lower vibrational levels can play a role in indirect DR. These states cause the structure in the DR cross sections discussed below.

## 2. Cross Sections and Rates

The full cross sections including the resonance states have been calculated using a Multichannel Quantum Defect Theory Approach (MQDT) (Guberman and Giusti-Suzor, 1991; Guberman, 1994) modified to handle the derivative couplings needed to describe Born-Oppenheimer breakdown and revised to handle multiple dissociative states and multiple values for the electron angular momentum. This approach handles both direct and indirect recombination simultaneously and allows both to interfere with each other. The MQDT approach is quite powerful and can handle large numbers of intermediate resonance states without difficulty. Interference between Rydberg vibrational levels belonging to different electronic states leading to "complex resonances" is fully described. The calculated cross section is shown in Figure 2. The direct cross section omits the resonance states, i.e. the vibrationally excited Rydberg levels, and is close to a straight line. The

sharp structure seen in the full cross section is due to the resonances that we label by  $(n,v,\ell)$  where  $n$  is the principal quantum number,  $v$  is the vibrational level and  $\ell$  is the angular momentum of the free electron. The structure at low energies is dominated by the  $(3,4,1)$  level near 0.014eV followed at higher energies by the  $(6,1,1)$ ,  $(3,6,0)$ ,  $(7,1,0)$ , and  $(4,3,0)$  levels. The rate is shown in Figure 3. The  $(3,4,1)$  level plays an important role in determining the shape of the plot. Above 20K, the full rate is above the direct rate due to the intermediate Rydberg resonance



**Figure 3.** The calculated direct (dashed) and full (solid) DR rates for  $^4\text{HeH}$ .

states. The full rate rises rapidly between 20 and 100K to a plateau between 100 and 300K. For  $200 < T_e < 400\text{K}$ , the rate is  $6.2 \times 10^{-9} \times (T_e/300)^{-0.14} \text{cm}^3/\text{sec}$ . We have also done calculations on  $^3\text{HeH}$ . The rate for  $^3\text{HeH}$  DR is  $2.6 \times 10^{-8} \times (T_e/300)^{-0.47} \text{cm}^3/\text{sec}$ . The rate increases as the isotopomer reduced mass decreases.

These results on both  $^4\text{HeH}$  and  $^3\text{HeH}$  have implications for  $\text{H}_3^+$ . For  $\text{H}_3^+$ , we can also expect that the lightest isotope, i.e.  $\text{H}_3^+$ , will have the highest rate compared to deuterium or tritium containing species. If we fuse two of the H atoms in  $\text{H}_3$  together we get the fictitious molecule,

$^2\text{HeH}$ . The full calculated rate for  $^2\text{HeH}$  is  $3.6 \times 10^{-7} \text{cm}^3/\text{sec}$  indicating that this mechanism in combination with light reduced masses can yield high DR rates. In  $\text{H}_3$ , in  $\text{C}_{2v}$  symmetry, attention will focus on the lowest  $^2\text{A}_1$  and  $^2\text{B}_2$  valence states formed by pulling apart the He in  $^2\text{HeH}$ . In summary, we have found that nonnegligible DR rates can occur even in cases where the dissociative curves do not cross the ion curve. Electron capture occurs by Born-Oppenheimer breakdown. Our calculations agree with both the CRYRING storage ring experiment (G. Sundstrom, et al., 1994) and with the TARN II (Tanabe et al., 1993) storage ring experiment that detects almost entirely  $\text{H}(n=2)$  dissociation products supporting our assignment of the  $\text{C } ^2\Sigma^+$  state as the primary dissociative route.

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